

**ALKALINITY AND pH MEASUREMENTS DURING THE
OVIDE 2010 ON BOARD R/V THALASSA
8 JUNE AND 8 JULY 2010**

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SCIENTIFIC REPORT

CO₂ variables Report

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Introduction

The carbon system is defined by four variables: pH, Total Alkalinity (A_T), partial pressure of carbon dioxide (pCO_2) and Total Inorganic Carbon (C_T). The knowledge of two of these variables allows calculating the other two by means of a set of equations deduced from thermodynamic equilibrium. During the OVIDE 2010 cruise pH and A_T measurements were sampled from bottle depths at selected stations (table 1) and analysed on board. Also, to check the internal consistence, 35 samples for C_T were also taken in 7 stations along the section and will be analysed at laboratory.

This report resumes the activities, methods and first results obtained during the OVIDE 2010 cruise. This cruise was carried out between 8 June and 8 July on board the R/V Thalassa.

Table1: Samples taken at each station for pH, Total Alkalinity (A_T) and Total Inorganic Carbon (C_T).

Station	pH	A_T	C_T	Station	pH	A_T	C_T	Station	pH	A_T	C_T
1	4	4		34	27			67	18	18	
2	8	8		35	28	24	5	68	17		
3	11	11		36	28			69	17	15	
4	15	12		37	27	23		70	18		
5	21	21		38	27			71	19	19	
6	24			39	27	24		72	21		
7	24	23		40	27			73	21	20	
8	26			41	26	24		74	22		
9	25	24		42	26			75	24	24	
10	28			43	26	24	5	76	25		
11	28	24		44	26			77	24	22	5
12	28			45	26	24		78	25		
13	28	24		46	24			79	24	22	
14	28			47	25	24		80	24		
15	28	24	5	48	26			81	24	22	5
16	28			49	25	14		82	23		
17	28	24		50	25			83	23	19	
18	28			51	25	24		84	21		
19	28	24		52	25			85	20	19	
20	28			53	25	24		86	19		
21	28	24		54	23			87	18	18	
22	28			55	26	24	5	88	16		
23	28	24	5	56	26			89	12	12	
24	28			57	25	24		90	8	8	
25	27	24		58	26			91	6		
26	26			59	23	23		92	5		
27	28	24		60	23			93	4	4	
28	28			61	23	23		95	4		
29	28	24		62	22			97	4	4	
30	27			63	22	19		98	5		
31	27	24		64	21						
32	27			65	21	18					
33	27	23		66	22						

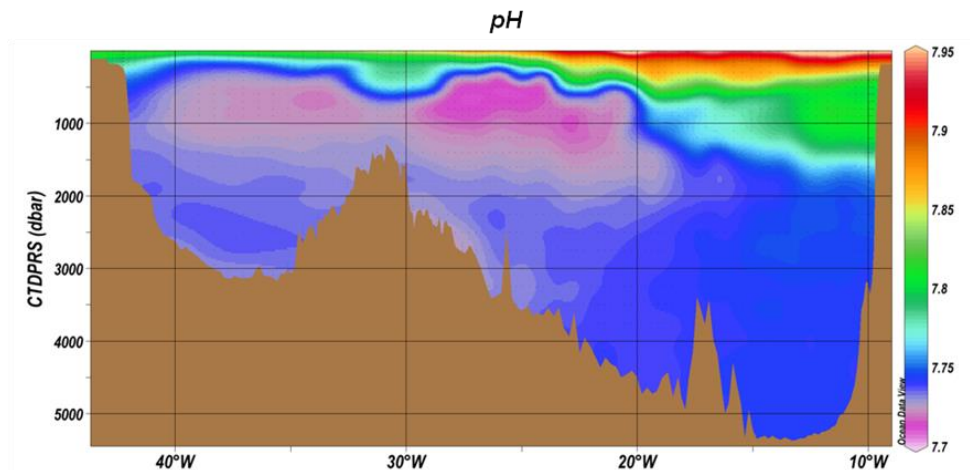
pH analysis

pH was measured spectrophotometrically following Clayton and Byrne (1993). This method consists on adding a dye solution to the seawater sample, so that the ratio between two absorbencies at two different wavelengths is proportional to the sample pH. Seawater samples for pH were collected at 95 stations after oxygen samples from depth using cylindrical optical glass 10-cm path length cells, which were filled to overflowing and immediately stopped. The indicator was a solution of m-cresol purple prepared in seawater. After sampling all the samples were stabilised at 25°C. All the absorbance measurements were obtained in the thermostated (25±0.2 °C) cell compartment of a SHIMADZU UV-2401PC spectrophotometer. Seawater pH was measured using a double-wavelength spectrophotometric procedure (Byrne, 1987). The absorbance was measured at three different fixed wavelengths (434, 578 and 730 nm) and 75 µl of the dye solution were added to each sample using an adjustable repeater pipette. pH, on the total hydrogen ion concentration scale, is calculated using the following formula (Clayton and Byrne, 1993):

$$\text{pH}_t = 1245.69/T + 3.8275 + (2.11 \cdot 10^{-3})(35-S) + \log((R-0.0069)/(2.222-R \cdot 0.133))$$

Where R is the ratio of the absorbencies of the acidic and basic forms of the indicator corrected for baseline absorbance at 730 nm ($R = A_{578}/A_{434}$), T is temperature in Kelvin scale and S is salinity. Here, 0.0047 pH units were added to the experimental pH values following the recommendations in DelValls and Dickson (1998) and Lee et al. (2000).

In order to check the accuracy of the pH measurements, samples of CO₂ reference material (CRM, batch 99, distributed by A.G. Dickson from the Scripps Institution of Oceanography) were analysed during the cruise. The accuracy of the method during the cruise using analysis of CRM (pH=7.929) was -0.0030 ± 0.0010 . The precision was determined, analysing 14 samples taken from different Niskin bottles closed at the same level (4815 dbar) at station 0. The precision was ± 0.0018 . The following figure shows pH distribution in the studied section.

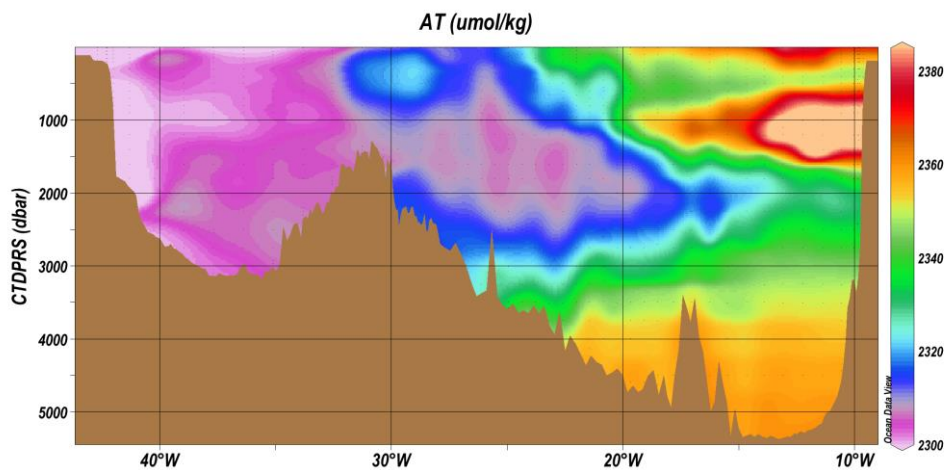


Alkalinity analysis

Total alkalinity was measured by potentiometric titrations to final pH of 4.40 following Pérez and Fraga 1987. Seawater samples for alkalinity were collected after pH samples, in 600 ml glass bottles. Samples were filled to overflowing and immediately stopped. Total alkalinity was measured using an automatic potentiometric titrator "TITRANDO Metrohm", with a combination glass electrode and a Pt-1000 probe (Metrohm 6.0257.000). The potentiometric titrations were carried out with hydrochloric acid ($[HCl] = 0.1 \text{ M}$, Riedel-deHaën, Fixanal 38285).

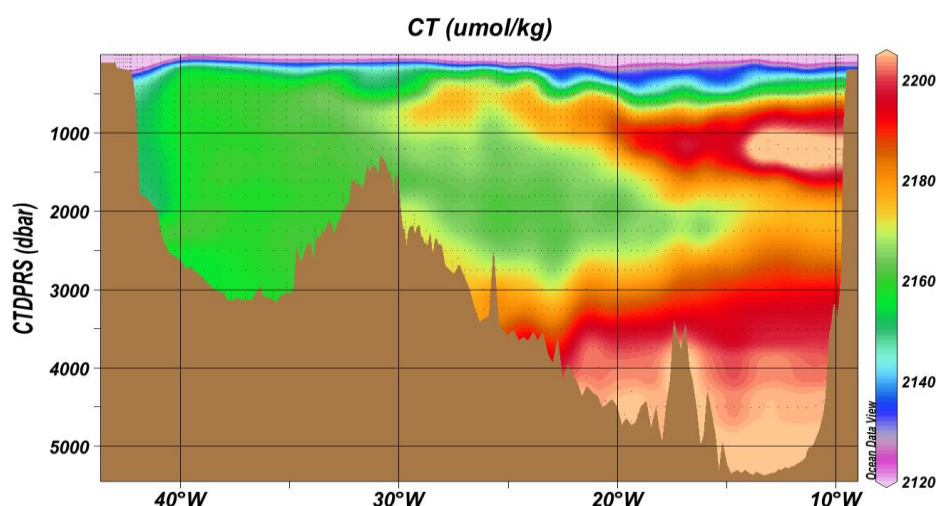
The electrode was standardised using a buffer of pH 4.4 made in CO_2 free seawater (Pérez et al., 2000). Concentrations are given in $\mu\text{mol/kg-sw}$. In order to check the exactitude of the A_T measurements, samples of CO_2 reference material (CRM, batch 99, distributed by A.G. Dickson from Scripps Institution of Oceanography) were analysed during the cruise. To check the precision a substandard (surface seawater stored into a container of 50L) was measured at the beginning and at the end of each batch of analyses. Each sample was analysed twice.

The precision of the A_T measurements ($\pm 0.34 \mu\text{mol}\cdot\text{kg}^{-1}$) was calculated analysing 14 samples for reproducibility taken from different Niskin bottles closed at the same level (4815 dbar) at station 0. Besides, the 1011 A_T duplicates analyses showed a reproducibility of $0.23 \pm 0.44 \mu\text{mol}\cdot\text{kg}^{-1}$ along the cruise. The distribution alkalinity along the section is shown in the following figure.

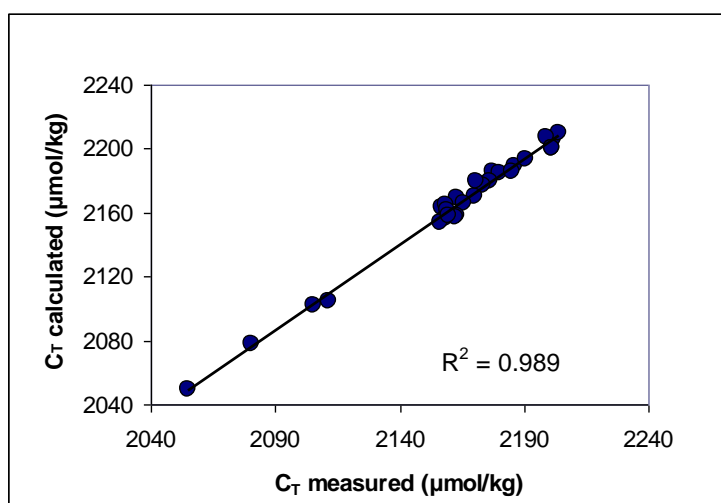


Carbono Inorgánico Total (C_T)

The C_T was calculated from pH and A_T using thermodynamic equations in seawater and the constants described by Mehrbach refitted by Dickson and Millero (Dickson and Millero 1987, Mehrbach et al. 1973) for carbonate, and Dickson (Dickson 1990) for sulphate. The distribution of calculated C_T along the section is shown in the following figure.



Besides, the 35 samples taken along the OVIDE section for C_T were analysed at laboratory using a SOMMA (single-operator multiparameter metabolic analyzers) connected to a Model 5011 coulometer (UIC). The sample fills an automated pipette. The contents of the pipette are pneumatically injected into a stripping chamber. Phosphoric acid (8.5%) was added to the sample. The resultant CO_2 is extracted, dried and coulometrically titrated. Calibration was performed by analyzing CRM. A good correlation ($R^2=0.989$) was found between measured C_T and calculated C_T .



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